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UNITED STATES DEPARTMENT OF AGRICULTURE
AGRICULTURAL RESEARCH SERVICE
Northern Regional Research Center
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Cap 3
MYCOTOXINS

Aflatoxin: Detection and Determination in Corn

Mycotoxins are toxic substances that may be produced by molds in corn under special circumstances in the field and in storage. The best known of these toxins and of potentially the greatest concern are the aflatoxins, a family of closely related substances. These substances can cause cancer and death in animals or result in lowered feed efficiency and weight gains; in humans there is circumstantial evidence for their involvement in causing liver cancers.

A number of analytical methods have been developed for the detection or measurement of these substances. These methods vary in purpose and complexity. Unfortunately, mycotoxins do not occur uniformly in contaminated corn, so adequate sampling and subsample preparation is necessary before meaningful assays of any type can be performed. Methods for aflatoxin analysis of corn can be divided into three categories: (1) Rapid presumptive tests to locate lots of corn that may contain the mycotoxin, (2) screening procedures to determine presence or absence of toxin, and (3) quantitative methods to determine amount of aflatoxin.

1. Presumptive test: This is a visual test that is used initially to locate lots that may be contaminated with aflatoxin. The corn sample (5-10 pounds) is examined under ultraviolet light (365 nm) for the presence of bright greenish-yellow fluorescing (BGY) particles. The glow observed has been compared to that of fireflies. The exact color should be compared to a chemical standard (available from the Northern Regional Research Center) that gives a similar fluorescence under ultraviolet light. Compounds in corn with other colors of fluorescence are not associated with aflatoxin. The substance responsible for the BGY glow in corn is not aflatoxin but a substance often produced by the mold that also makes the toxin. Corn should be cracked before inspection under the ultraviolet light (365 nm) to make sure no BGY material is missed.

Occurrence of a BGY "positive" test should be interpreted with care because fluorescence is not always accompanied by the presence of aflatoxin. Fluorescence should be interpreted as a warning that more definitive tests are required.

The table summarizes the results of analyzing BGY positive and negative samples:

Aflatoxin content (% of corn samples)			
BGY Test	Quantitative Analysis		
	Negative	Less Than 20 p.p.b.	20 or More p.p.b.
Negative (cracked corn)	99	1	0
Positive (at least one BGY particle per 10 pounds)	45	28	27
Positive (more than 20 BGY particles per 10 pounds)	5	30	65

Inspection of corn for BGY pinpoints about twice as many samples for analysis as are actually found to contain measurable amounts (1-3 p.p.b.) of aflatoxin. Use of the fluorescent test to minimize the analytical workload obviously would have more value at low levels of incidence than at high levels. For example, the 2-3% incidence observed in early surveys of Midwest market corn would give rise to about 4-6% of the samples which would require analysis because of positive BGY tests. The advantages over analysis of all samples is obvious under these circumstances.

2. Screening procedures: A small glass column (the minicolumn) containing appropriate adsorbents such as Florisil or silica gel may be used as a quick screening procedure to detect the presence or absence of aflatoxin at a predetermined level (for example, 20 p.p.b.). It does not actually give the level of the toxin present, although rough estimates are sometimes made by skilled operators. The test requires 0.3 to 1 hour to run, excluding sample preparation; false positives generally do not occur.
3. Quantitative methods: These procedures are lengthy (3 hours), somewhat complex, and unsuited for field purposes because they require more complicated equipment. However, they do give a measurement (down to 1-3 p.p.b.) of the amount of aflatoxin present. In this country the procedure recommended by the Association of Official Analytical Chemists and the American Association of Cereal Chemists is the so-called CB method. It must be performed by skilled analysts in fairly well-equipped laboratories. Some of the analytical methods developed for commodities other than corn--peanuts and cottonseed--give very low aflatoxin recoveries.

The ultraviolet light (365 nm) used in the presumptive test can be obtained from various suppliers, some of whose addresses* follow:

Ultra-Violet Products, Inc.
Walnut Grove Avenue at Grand
P.O. Box E
San Gabriel, California 91778

LaPine Scientific Co.
6001 South Knox Avenue
Chicago, Illinois 60629

Cole-Parmer Instrument Co.
7425 North Park Avenue
Chicago, Illinois 60643

Scientific Products
1210 Leon Place
Evanston, Illinois 60201

Seedburo Equipment Co.
1022 West Jackson Blvd.
Chicago, Illinois 60607

Applied Science Laboratories, Inc.
P.O. Box 440
State College, Pennsylvania 16801

Spectronics, Inc.
24-A Kinkel Street
Westbury, New York 11590

Descriptive literature and current prices may be obtained by writing directly to the companies.

*The mention of company names is for convenience only and does not imply the Department's endorsement of their products.

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SERIAL RECORDS

Curing-Antiscaling Emulsion for Concrete

After 1-2 years the pavement should be treated periodically with linseed oil (19). Such treatment may already be standard practice for pavement in some locations. Standard practice is to use the most economical form of linseed oil as an antiscaling agent. Previously, linseed oil dissolved in a mineral spirits solvent has served this purpose (16). However, such a solution is flammable, contains petroleum solvents, and is not a curing agent. The lack of flammability of the emulsion makes it preferable over the solution for coating enclosed areas, such as basements and underground garages.

Weight %

Oil phase (50 + 1 volume %)	
Boiled linseed oil	97.0 + 1
Saturated tallow alcohols	3.0 + 1
Water phase (50 + 1 volume %)	
Water	99.60 + 0.01
Sodium hydroxide	0.37 + 0.01
Dipicolinic acid	0.03 + 0.001

A note of caution: Do not add the water phase to the oil phase and do avoid beating in air while mixing. Finally, the emulsion is pumped through a two-stage homogenizer (such as one made by Manton-Gaulin or by Cherry-Burrell) at 4,000 p.s.i. The emulsion is stable through more than five freeze-thaw cycles (a cycle is 70° to 0° to 70° F) and remains stable for more than 2 years.

According to laboratory tests, alternate formulations (10) yielding reduced water loss during curing and more durability afterwards can be obtained by substituting heat-bodied linseed oil or tung oil for 20 percent of the boiled linseed oil in the oil phase of the original emulsion. The heat-bodied linseed oil should have a Gardner Holdt viscosity Z8 (40,000 to 50,000 centipoises Brookfield).

Water Retention: The NRRC emulsion passes the ASTM:C156 Water Retention Efficiency of Liquid Membrane-Forming Compounds for Curing Concrete (17), when it is applied at 175 square feet per gallon. The maximum loss allowed in this test is 0.055 gram per square centimeter per 72 hours. Five different commercial batches tested as follows: 0.044, 0.055, 0.045, 0.043, and 0.040 gram per square centimeter per 72 hours.

The alternate emulsions (10) meet the ASTM test at 200 square feet per gallon with losses as low as 10 to 22 milligrams per square centimeter. They also pass the U.S. Army Corps of Engineers CRD-C302-68 Method of Test for Sprayability and Unit Moisture Loss Through the Membrane Formed by a Concrete Curing Compound. It is being determined in the field whether increased durability justifies the slightly greater cost of these formulas.

Curing Application: The emulsion should be applied as soon as the concrete is finished (broomed, dragged, or troweled). The preferred method of application is with an airless spray gun or a wand like that used for orchard spraying. An ordinary paint spray gun can be used with an air pressure of about 30 p.s.i.

The nominal rate of application is 175 square feet per gallon for broomed surface concrete (200 square feet per gallon for the alternate emulsions).

Antiscaling Application: If the emulsion is intended as an antiscaling agent, it should be applied when the concrete is at least 2 weeks old and preferably 4 weeks. It can be applied with beneficial results to older concrete, even to surfaces that have started to scale. Any surface should be clean and dry before coating. Two coats are preferable to gain more uniform application. The coats should total about 225 square feet per gallon for both boiled linseed oil and alternate emulsions. Rate of application depends on porosity and roughness of the concrete surface. Care should be taken to avoid an excess of oil because this condition will temporarily lower wet skid resistance (12).

Abrasion Resistance: When applied as a curing compound, the NRRC emulsion slows down hardening of the surface. Light traffic is permissible (such as that required to cut joints) in 5 to 24 hours, but heavy traffic should be kept off for 72 hours. At 28 days, hardness is normal and continues to increase thereafter. Research at the Northern Regional Research Center tends to confirm results reported by the California Division of Highways (3), which states that linseed oil increases the abrasion resistance of concrete more than any other material tested.

Penetration: The penetration of linseed oil curing and antiscaling compounds into the surface of concrete may be related to their ability to protect concrete from freeze-thaw cycles and deicing chemicals (13,18). On the one hand, conventional curing agents, which do not protect, tend to form a film on the surface and do not penetrate into the concrete. On the other hand, linseed emulsions penetrate when used as either a curing or antiscaling agent. The Northern Regional Research Center, in cooperation with the National Flaxseed Processors Association, has developed a simple test for determining penetration of linseed emulsions and solutions into concrete (6,7).

Practical Studies on Sidewalks: NRRC's linseed oil emulsion has been used to cure concrete sidewalks in Peoria, Ill., and in Washington, D.C. (11,14). Applications at the Northern Regional Research Center in April, May, and June 1963, were the first outside curing tests. The results were reported as "pop-outs" within 100 square feet. A piece of concrete pops out apparently when a porous rock beneath the surface absorbs water, freezes, and expands. After 39 applications of salt on sidewalks between the spring of 1963 and the spring of 1965, emulsion-cured concrete averaged 20 pop-outs; membrane-cured concrete, 152; plastic-cured concrete, 157; and air-cured concrete, 222.

That part of the Washington, D.C., sidewalk cured under polyethylene sheeting has had to be replaced because of damage from heavy salting. The linseed oil emulsion-cured area is still in excellent condition.

Curing of Bridge Decks and other Concrete Structures: In 1966, engineers from Wichita, Kansas, specified the NRRC emulsion for city construction. It has now been placed on a total of 11 projects in Kansas under weather conditions varying from freezing to hot and windy.

In 1970, the Oklahoma State Highway Department (1,2,15) became the first to specify curing bridge decks with the oil-in-water emulsion developed and patented by NRRC. Concrete in 138 bridges was emulsion-cured after Oklahoma began tests in 1968 in cooperation with the U.S. Department of Agriculture and the U.S. Department of Transportation. Emulsion curing was specified for 25 bridge contracts let between December 1970 and May 1971. Ten or more states have cured bridge decks and other highway structures with NRRC emulsion, including 6 million square feet of shoulders on Interstate 94 in the Chicago and Milwaukee areas during 1974. Private contractors used NRRC emulsion on parking decks (Chicago O'Hare Airport, 5 million square feet), ramps, and roadways. ARS agencies used NRRC emulsion on cattle feed lots, grain storage bins and other farm structures. General Services Administration and the Navy Department are including NRRC emulsion in their specifications on new construction. Shortages in petrochemicals have focused attention on replacing linseed oil in mineral spirits antiscaling compound now used extensively on highways with NRRC emulsion.

Emulsion Curing and Interaction with Later Treatments: A linseed oil coating increases adhesion of traffic paints. Bituminous overlay can be made on linseed oil-treated concrete with no loss of adhesion if a tack coat is first applied. Carborundum and other finishes can be put on concrete that has been cured with linseed oil emulsion.

Savings: In addition to increasing the life of concrete, Table 1 illustrates savings in labor and materials resulting from the linseed oil emulsion method of curing and protecting concrete. Although costs vary widely, about \$1.00 a square yard is saved by applying a linseed oil emulsion instead of moist curing followed by a linseed oil antiscaling treatment. If membrane curing is followed by linseed oil antiscaling treatment, the saving is slightly less. One company using the emulsion exclusively to cure outdoor concrete estimates its savings between \$0.79 to \$0.81 per square yard. The contractor returned \$0.26 per square yard to the company on his first use of the emulsion method.

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Mention of firm names or trade products is made for information only and does not imply that they are endorsed or recommended by the U.S. Department of Agriculture over other firms or similar products not mentioned.

Table 1.--Concrete Curing, Protecting Comparisons

Wet curing, followed 30 days ^{1/} later with antiscaling steps	Membrane curing, followed 30 days ^{1/} later with antiscaling steps	Linseed emulsion curing- antiscaling 5 hours ^{1/}
CURING		
1a. Spread plastic sheets, burlap mats as soon as they will not mar concrete surface, usually about 5 hr after placing concrete	Spray with curing compound when free water disappears. Leaves concrete ready for sawing. May interfere with painting (traffic lines) and finishing	Spray with linseed oil emulsion as soon as free water disappears, immediately to 5 hr after placing. Leaves concrete ready for sawing, painting (lines), or finishing. Protects against freeze-thaw damage after 2 years. Eliminates 6 steps
1b. Burlap must be kept wet by repeated spraying with water (extra steps)		
SAWING		
2. Remove plastic or burlap 5 to 24 hr after placing concrete	2. Eliminated	2. Eliminated
3. Saw joints	3. Saw joints	3. Saw joints
4. Replace plastic or burlap immediately (sometimes forgotten)	4. Eliminated	4. Eliminated
5. Plastic or burlap usually removed at end of 3 days to get it out of the way. Longer curing better	5. Eliminated	5. Eliminated
ANTISCALING PROTECTION--THREE EXTRA STEPS		
6. About 30 days after step 1a or 1b concrete is cleaned	6. Cleaning as in wet curing	6. Eliminated
7. First application of flammable antiscaling compound	7. First application of antiscaling compound as in wet curing	7. Eliminated
8. Second application of flammable antiscaling compound	8. Second application of antiscaling compound as in wet curing	8. Eliminated

^{1/} Time elapsed between placing of concrete and start of final three steps.

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INSOLUBLE STARCH XANTHATE (ISX)

Preparation and Use in Heavy Metal Recovery

A water-insoluble starch xanthate (ISX) offers industry a low-cost product that removes and recovers heavy metals from wastewater. Previously, heavy metals had been effectively removed with a starch xanthate-cationic polymer complex (1-4) that allows metal recovery, but almost all cationic polymers are expensive. More traditional removal methods based on inorganic precipitation with lime, alum, or iron salts leave a sludge often placed in landfills. Leaching of the unrecovered metal to underground water and loss of metal resources result. Although precipitation as inorganic salts is inexpensive, recovery of the heavy metal for recycling is difficult.

Starch xanthate made from unmodified corn or wheat starch (5-8) is water soluble. Starch xanthate itself precipitates large amounts of mercury(II), but because almost all other metal xanthate salts are more soluble, removal is not so efficient as when a cationic polymer is included. The efficiencies of metal removal by starch xanthate alone can be greatly increased if the initial starch is crosslinked. Xanthation of a highly crosslinked starch gives an insoluble product. The addition of magnesium sulfate during the preparation affords (a) increased filtration or centrifugation rate, (b) increased flash drying efficiency, (c) increased room temperature stability and (d) increased settling rate in heavy metal ion removal. Other soluble magnesium salts are also effective as long as the grams of magnesium ion: %S in product is 0.4:1. ISX lowers the concentration of practically all heavy metal cations to levels below strict discharge limits (9-12).

Laboratory Preparation

A highly crosslinked starch (100 g.) is slurried in water (435 ml.), and sodium hydroxide (45 g.) in water (125 ml.) is added. This mixture is stirred 30 minutes. Carbon disulfide (30 ml.) is added and the mixture is stirred 1 hour in a covered beaker. Magnesium sulfate (19 g.) in water (250 ml.) is added and the mixture is allowed to stir an additional 5 minutes. The slurry is filtered through a Büchner funnel using Whatman No. 54 filter paper and the solid is washed with water (1,000 ml.). The solid (75% H₂O) is then washed with acetone and ether. After drying for 2 hours under vacuum, the product was analyzed. Yield 120 g.; S, 9.62%; H₂O, 8.92%; ash 12.89%.

Weights of reactants and analyses of the products for several preparations are found in Table 1. The yellow-tan product should be stored in a dry place at 0 to 30° C. for maximum effectiveness. Under these conditions, flash-dried products of less than 3% moisture showed very little change over several months storage at room temperature.

Table 1.--Preparation and Analysis of Insoluble Starch Xanthate

Cross-linked ¹ Starch	Carbon Disulfide, ml.	Magnesium ² sulfate, g.	% S d.b.	% H ₂ O ³	% Ash ⁴	Na, ⁵ mg.	Mg., ⁵ mg.	Na/Mg.	Capacity, meq/g.
A	15	12.4	5.76	2.19	10.72	8.5	6.2	1.37	0.88
A	20	15	7.44	1.34	16.52	10.6	6.9	1.54	1.14
A	25	17	8.70	1.40	19.20	12.1	7.0	1.73	1.20
A	30	19	10.12	0.85	24.08	14.2	7.4	1.92	1.56
A	35	21.5	8.86 ₇	1.74	18.15	13.2	8.3	1.59	1.36
A	30	18 ₆	8.05 ₇	1.33	13.31	11.4	7.1	1.60	1.24
B	30	18 ₆	9.29 ₇	0.86	16.32	12.8	7.3	1.75	1.44

- ¹ A. Epichlorohydrin crosslinked starch (HPD-53-91E, The Hubinger Company, Keokuk, Iowa). 9.09% H₂O; 100 g. (0.56 mole, dry basis).
- B. Vulca 90 (National Starch and Chemical Corp., Bridgewater, N.J.). 11.0% H₂O; 100 g. (0.55 mole, dry basis). Additional water may be required to promote easy stirring with Vulca 90.

² Approximately 2 g. magnesium sulfate for each 1% S in the product is optimum.

³ These products were flash dried; therefore, lower moisture values were obtained over solvent drying.

⁴ % Ash includes sodium and magnesium of xanthate and bound alkali in product.

⁵ A 0.25-g. sample was treated with 1 N HNO₃ (45 ml.) to remove all the sodium and magnesium. The filtrates diluted to 1 liter and Na and Mg concentrations were determined on a Varian Techtron AA 120 spectrophotometer.

⁶ Magnesium sulfate (18 g.) in water (180 ml) was added 45 seconds after the carbon disulfide and the reaction was allowed to proceed 1 hour.

⁷ Lower sulfur values were due to the additional water used in the preparation.

One-Step Crosslinking and Xanthation of Starch

Commercial corn starch (100 g., 10% H₂O) is slurried in water (150 ml.) containing sodium chloride (1.5 g.) and epichlorohydrin (7.0 ml.). To this slurry is added potassium hydroxide (6 g.) in water (40 ml.) slowly over 30 minutes and the mixture is allowed to stir for 16 hours. The suspension now containing the highly crosslinked starch can be xanthated as previously described after the addition of water (245 ml.).

Continuous Preparation of ISX

Crosslinked starch (20 lb., d.b.) is slurried in water (80 lb.) and magnesium sulfate (3.61 lb.) is added. The slurry is pumped through a Baker Perkins Flowmaster Rotofeed (7-1/2 in.) at 890 g./minute and 28° C. The sodium hydroxide (4.66 N, 24 liters) is metered in at 470 ml./minute and the carbon disulfide (3.32 liters) at 65 ml./minute. The slurry is pumped through in 50 minutes and after 30 minutes in a holding tank, water (10 gal.) is added for easier feeding to the centrifuge. The mixture is centrifuged in a Tolhurst Centrifuge (26 in.-2400 r.p.m.) at 650 r.p.m. and then washed with water (26.5 gal.). The cake is dewatered to 27% solids at 1,500 r.p.m. The cake is flash dried and gives the following analysis. S, 9.14%; ash, 14.06%; H₂O, 3.16%.

Insoluble starch xanthate prepared commercially can be made in large reactors as previously described or it can be made continuously via Rotofeed, followed by centrifugation, washing, and flash-drying. Commercially prepared products might require minor changes in reactant ratios to obtain maximum reaction efficiency.

Heavy Metal Removal

The optimum product for heavy metal removal appears to be the preparations using 30-ml. carbon disulfide with 18-20 g. magnesium sulfate. These products contain both a sodium xanthate and magnesium xanthate. For use in heavy metal removal the product should be added to the effluent (pH 3 or above) as a solid or slurry allowing the pH to rise to above pH 7 for optimum removal (Tables 2-3). The metal-xanthate sludge settles rapidly in the quiescent state in batch-type operations. For continuous-flow effluent streams the aid of a clarifier, centrifuge or filter should be used. The sludge obtained from a centrifuge or filter is 50% solids which allows handling ease. After 3 hours under ambient conditions, solids increase to about 90%.

Table 2.--Removal of Heavy Metal Cations from Water with Insoluble Starch Xanthate

Metal	Initial Conc., mg./liter	ISX, g.	Residual Conc., mg./liter	Illinois Discharge Limit, mg./liter
Ag ⁺	53.94	0.32	0.016	0.005
Au ⁺³	30.00	0.50	<0.010	---
Cd ⁺²	56.20	0.64	0.012	0.050
Co ⁺²	29.48	0.64	0.090	---
Cr ⁺³	26.00	0.64	0.024	1.0
Cu ⁺²	31.77	0.32	0.008	0.020
Fe ⁺²	27.92	0.32	0.015	1.0
Hg ⁺²	100.00	0.64	0.001	0.0005
Mn ⁺²	27.47	0.64	0.015	1.0
Ni ⁺²	29.35	0.64	0.160	1.0
Pb ⁺²	103.60	0.64	0.035	0.100
Zn ⁺²	32.69	0.32	0.294	1.0

Solutions (1,000 ml.) containing the individual metals at the indicated concentration were treated with the indicated amount of ISX (capacity = 1.56 meq/g.) at pH = 3.7. Solutions were stirred for 5-60 min. at a final pH of 8.9. After filtration, the residual metals were determined by a Varian Techtron AA 120. The theoretical weight of ISX for a divalent metal is 0.64 g. Values listed with less than (<) were below detection limits.

Table 3.--Removal of Metals from Dilute Solution with Insoluble Starch Xanthate

Metal	Initial Conc., mg./liter	Residual Conc., mg./liter
Cd ⁺²	5.62	0.001
Co ⁺²	2.95	<0.010
Cr ⁺³	2.60	0.026
Cu ⁺²	3.18	<0.005
Fe ⁺²	2.79	0.001
Hg ⁺²	10.00	0.0007
Mn ⁺²	2.75	0.010
Ni ⁺²	2.93	<0.050
Pb ⁺²	10.36	<0.031
Zn ⁺²	3.27	0.007

A solution (1,000 ml.) containing a mixture of heavy metals of the indicated concentrations at pH 3.5 was treated with ISX (capacity = 1.56 meq/g., 0.32 g.) to a final pH = 8.9. After filtration the residual metals were determined by a Varian Techtron AA 120. Values with less than (<) were below detection limits.

Stoichiometric quantities of ISX at a pH above 7 will in most cases reduce heavy metal concentrations to below established discharge limits. In some cases, less than stoichiometric quantities of ISX give excellent removal. Heavy metal removal is instantaneous; however, longer contact times are not detrimental to removal and in most cases increase removal. Salt (NaCl) concentrations of 0-10 percent have little influence on the effectiveness of the method.

The effluent after treatment contains only sodium and magnesium ions from the product. There is no detectable sulfur byproduct unless a decomposed ISX is used. The use of an ISX product which has decomposed slightly will sometimes turn the effluent pink-amber, but at a pH above 8.5 these metal-bearing decomposition products precipitate leaving a clear effluent. If metal recovery is warranted, the metals can be released from the ISX by treatment with nitric acid to yield a concentrated solution of the metal ions. The sludge can also be incinerated to recover the metal oxides. In either treatment, the xanthate group is lost for further use. The nitric acid treatment does allow recovery of the crosslinked starch. If the sludge is landfilled, the metal is bound fairly strong and would have less chance to be leached out than with a hydroxide sludge. The metal ions are so tightly bound to the ISX that normal eluting agents are ineffective in metal release.

A preliminary cost-to-make estimate (April 1976 prices), based on laboratory studies for a dry ISX containing 9-10% S is \$0.30/pound, and this product has a metal binding capacity of 1.4-1.6 meq. of metal ion/g. product.

Stability studies of these products are presently underway. If the samples are kept cold (0-5° C) they are stable for at least 1 year. Room temperature stability (20-30° C) is somewhat less.

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MICROBIAL POLYSACCHARIDES 51.20 //

Information on Polysaccharide YB-4163

This product, from the research efforts of a team of microbiologists and carbohydrate chemists, is one of a series of polysaccharides made by fermentation processes developed at the Northern Laboratory. ✓

Information presented here is preliminary and is subject to further confirmation and extension as current research progresses and as industrial evaluation justifies. At present, research on polysaccharide YB-4163 has been restricted to preparing sufficient material for in-house studies on composition and properties.

Nature and Origin: An extracellular, high-molecular-weight polysaccharide produced by the black yeastlike fungus, Rhinochlamydomonas elatior Mangenot NRRL YB-4163. ✓

Preparation: Fermentation of a medium containing 3-5 percent commercial dextrose, organic nitrogen, dibasic potassium phosphate, and magnesium and zinc ions. Incubation is for 6-8 days at 25° C., aerobic conditions; final viscosity of culture is 3,000-5,000 centipoises.

Purification and Isolation: Centrifugation to remove cells, precipitation by ethanol in the presence of electrolyte (such as potassium chloride), reprecipitations, and finally dehydration by freeze drying. Other methods of purification are under investigation. Under experimental conditions to date, yields of purified product as the K-salt have been about 10 percent based on D-glucose.

Composition: Polysaccharide YB-4163 is composed mainly (more than 92 percent) of 2-acetamido-2-deoxy-D-glucuronic acid (GlcNAcUA). A neutral sugar portion (5 percent) of crude polysaccharide YB-4163 appears to be a contaminant that is associated with black pigment which gives the isolated product a grey color. Pigment-free preparations can be obtained.

Properties:

Gum Form: When precipitated from solution with 2 volumes of ethanol (95 percent), the partially dehydrated fibrous, cohesive material winds on the stirrer.

Solid Form: As now prepared on a bench scale, the freeze-dried solid is off-white to dark grey. When equilibrated under conditions of 50 percent relative humidity at 20° C., the solid contains 20 percent moisture.

Aqueous Solutions: Concentrated solutions (e.g., 1 percent) of polysaccharide YB-4163 are extremely viscous and display elastic behavior, i.e., the entire solution clings together and flows as a unit. Solutions also show pseudoplastic rheological behavior at high shear stress, whereas at low stress they exhibit plastic behavior (see Figure 1). The pH of the salt form is 5.7. Pigmented preparations give grey-brown transparent solutions. Removal of pigment results in water-clear solutions.

Specific Optical Rotation: $[\alpha]_D^{25} -75^\circ$ (c, 0.5, H₂O).

Neutral Equivalent: 255 (pKa = 3.67).

Film Formation: When cast upon suitable plates, aqueous solutions (1 percent) of polysaccharide YB-4163, dry to cohesive, flexible films. Test values (Table 1) are compared with those from polysaccharide B-1459, which is commercially available under the generic name "Xanthan" (produced by Xanthomonas campestris strain NRRL B-1459), and also from corn amylose.

Table 1. Physical Tests on Polysaccharide Films^{1/}

Polysaccharide	Glycerol, Percent	Tensile Strength, kg/mm ²	Elongation, Percent	Schopper Double Folds
YB-4163	0	5.9	3	17
	15	3.3	6	34
B-1459 (Xanthan)	0	5.8	3	6 ^{2/}
	15	4.0	4	43 ^{2/}
Corn amylose	0	7.2	13	900
	15	5.4	20	280

^{1/} One percent solutions were cast on flat plates and allowed to air dry.

^{2/} Heating the solution to 80° C. before pouring on the plate would increase the number of double folds.

Stabilization of Emulsions and Foams: Polysaccharide YB-4163 stabilizes oil-water emulsions. In Table 2, its ability to stabilize emulsions is compared with that of another black yeast polysaccharide (NRRL strain Y-6272) and xanthan. As a stabilizer of emulsions, polysaccharide YB-4163 at the total concentration of 0.3 percent is as good as or better than xanthan, considered an excellent emulsion stabilizer.

Table 2. Emulsions Containing 0.3 Percent Polysaccharide in Equal Parts of Oil and Water^{1/}

Oils	Polysaccharide		
	YB-4163	Y-6272	Xanthan
Paraffin	++	+	++
Soybean and cottonseed ^{2/}	+	+	-
Soybean ^{3/}	+	+	++
Corn ^{4/}	++	+	-
Olive	++	+	-
Safflower	+	+	-

^{1/} ++ = After 24 hours, 100 percent emulsion.
 + = After 24 hours, some emulsion.
 - = After 24 hours, no emulsion.

^{2/} Wesson[®], Hunt-Wesson Foods, Inc.

^{3/} Crisco[®], Procter and Gamble.

^{4/} Mazola[®], Best Foods.

Polysaccharide YB-4163 also stabilizes foams since near the end of the fermentation process, when a suitable amount of product has formed, the culture fluid becomes a thick stable foam.

Viscosity Relationships*: The viscosity-shear rate curves for various concentrations of polysaccharide YB-4163 are shown in Figure 2. Solutions are highly viscous, shear thinning, and nonthixotropic (i.e., when the shearing force is removed, the solutions rapidly regain their initial viscosity).

The shear stress-shear rate-viscosity relations were established by the method of T. C. Patton [J. Paint Technol. 38:656 (1966)] (Figure 1).

* All viscosity measurements were made with Brookfield viscometers. Data in Figures 2-5 were obtained with Model LVT, the appropriate spindle, at 30 r.p.m. and 25° C. unless otherwise noted. Data in Figures 1 and 6 were obtained with Model RVT, cone and plate, viscometer 1 r.p.m. (3.84 sec.⁻¹) and 25° C. unless otherwise noted.

According to this scheme, polysaccharide Y-6272 would be classified as a typical pseudoplastic material throughout the shear rate range, but polysaccharide YB-4163 is not. It has an inflection at about 0.1 sec.^{-1} where it changes from pseudoplastic to plastic. It thus is a hybrid type. Although xanthan is a hybrid also, it tends to have more plastic behavior.

Salt affects viscosity of solutions of polysaccharide YB-4163 (Figure 3). The behavior seen for KCl is representative of CaCl_2 also. Most divalent and trivalent ions tend to precipitate the polysaccharide.

At high temperatures viscosity of 1 percent solutions in the presence and absence of KCl is lowered (Figure 4), but on cooling viscosity is regained. Samples were heated for extended time periods at designated temperatures (with or without KCl) and then cooled to 25°C. before measuring viscosity (Figure 5).

Viscosity remains unchanged in the pH range of 5 to 10 (Figure 6). Viscosity decreases at higher or lower pH's.

Applicability: Polysaccharide YB-4163 possesses a unique constitution, and its properties make the polysaccharide suitable for industrial applications, because: (1) it is water soluble, (2) it forms flexible films, (3) it stabilizes oil-water emulsions, and (4) it stabilizes foams. Although some individual samples have exhibited behavior even superior to that reported here, including more tolerance to salt and heat, the data given are considered representative at present.

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Shear Stress - Shear Rate - Viscosity Relationship (25°C)
1% Polysaccharides

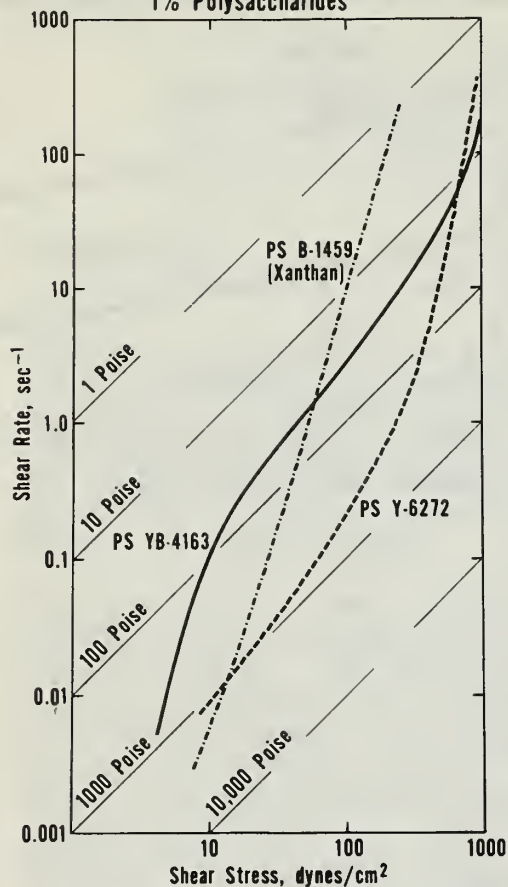


Fig. 1

Shear Rate - Viscosity Curves for Various Concentrations
of Polysaccharide YB-4163

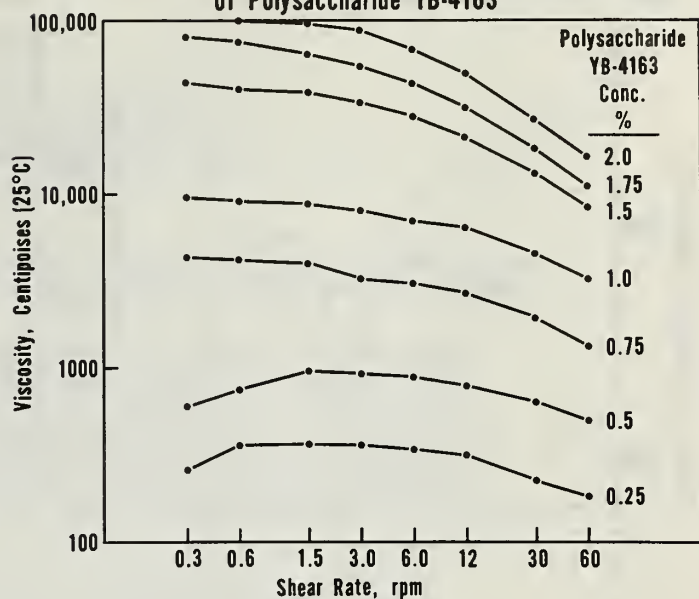


Fig. 2

Salt - Viscosity Relationship (25°C) for Various Concentrations
of Polysaccharide YB-4163

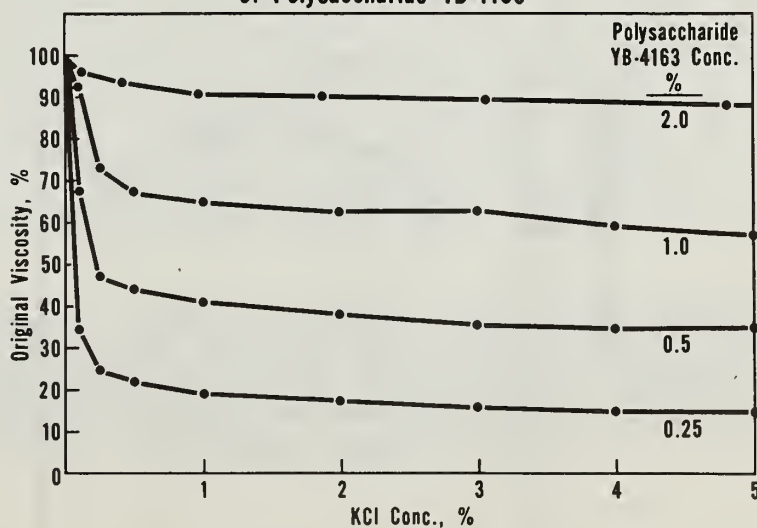


Fig. 3

Temperature - Viscosity Relationship
1% Polysaccharide YB-4163

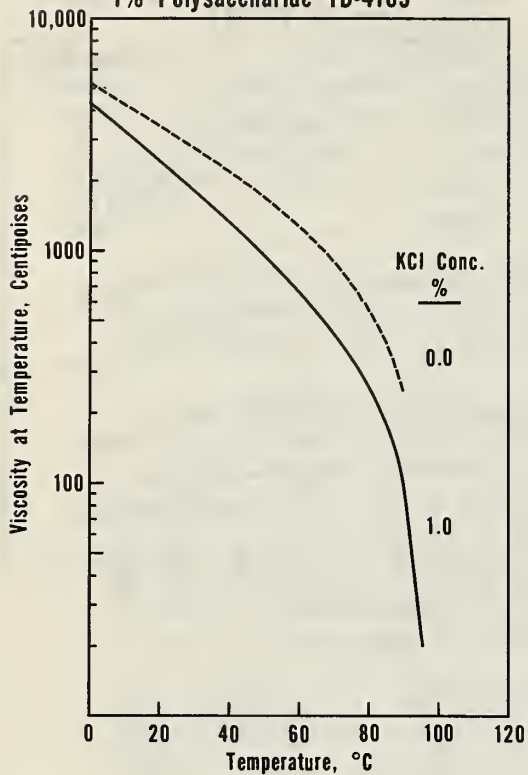


Fig. 4

Extended Heating - Viscosity Relationship
1% Polysaccharide YB-4163

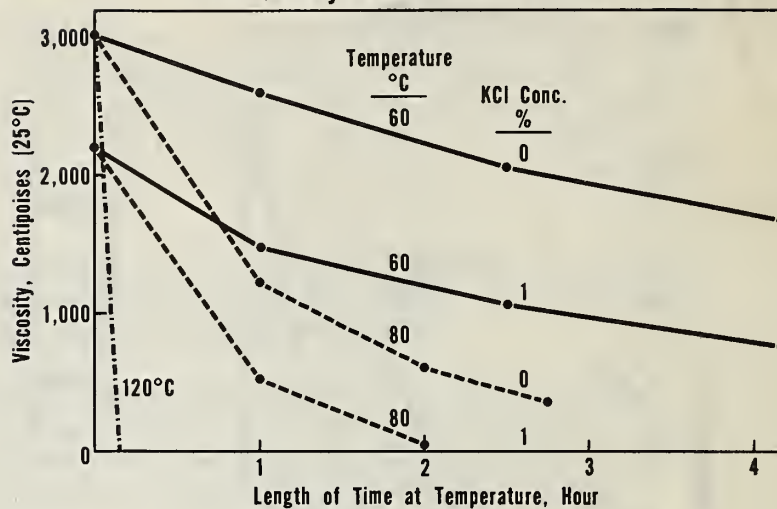


Fig. 5

pH - Viscosity Relationship
1% Polysaccharide YB-4163

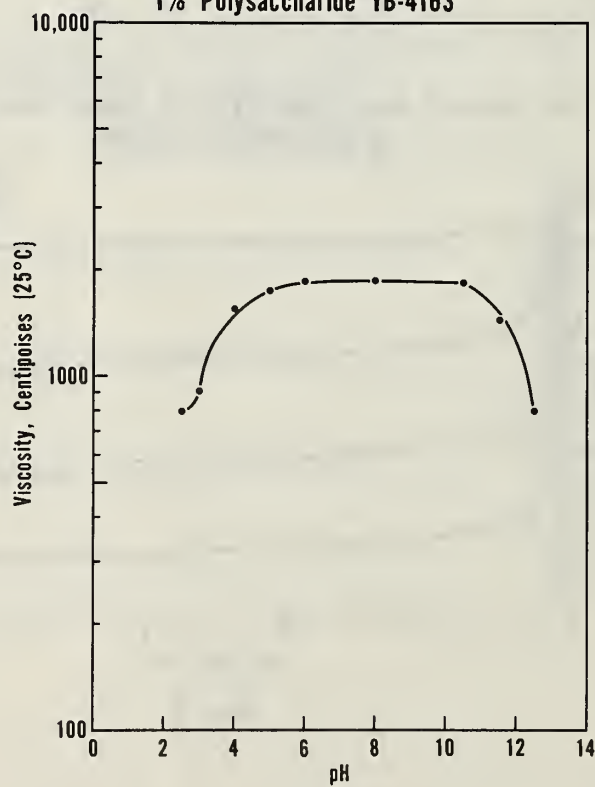


Fig. 6

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UNITED STATES DEPARTMENT OF AGRICULTURE
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Northern Regional Research Laboratory
Peoria, Illinois 61604MYCOTOXINSAflatoxin: Detection and Determination

Methods of aflatoxin analysis of corn fall into three categories:

- (1) Visual inspection of kernels under black light or ultraviolet light (365 nm.) serves to locate lots that may contain aflatoxin.
- (2) Rapid screening procedures determine the presence or absence of the toxin, but they do not determine the levels of toxin present.
- (3) Finally, rather lengthy procedures are available to measure actual amounts of toxin in corn.

Corn is inspected under black light for a characteristic bright greenish-yellow fluorescence associated with aflatoxin in broken and damaged kernels. The test takes 5 minutes. If fluorescence is observed, aflatoxin may be present but not necessarily in appreciable or detectable levels. The bright greenish-yellow fluorescence is not caused by aflatoxin; rather it is caused by another compound produced by the mold along with aflatoxin. The fluorescence on corn is not stable and will fade in 4 to 6 weeks if the sample is exposed to ordinary light and more quickly with ultraviolet light. Therefore, a chemical with the same fluorescence as that when inspecting corn under black light is used as a standard. This chemical must be sealed in a vial because moisture in the air changes the color of its fluorescence from bright greenish-yellow to pale blue.

If corn is found to contain kernels or pieces with the bright greenish-yellow fluorescence, it must be analyzed to determine whether aflatoxin is present or not. Although rapid screening procedures detect the toxin, they do not have the capability of determining exact amounts. Rapid procedures take about 20 minutes. An extract of corn is prepared, placed on a chromatographic column, and then inspected under black light. Aflatoxin fluoresces a pale blue, a color that can be observed on the chromatographic column if the corn contains more than 5 to 10 p.p.b. of toxin.

To determine amounts of aflatoxin in corn, rather lengthy quantitative procedures are available that will determine levels of toxin as low as 1 to 3 p.p.b. Measurements of amounts of aflatoxin on quantitative thin-layer chromatographic plates of corn extracts are based on the pale blue fluorescence of the actual compound.

The reliability of all three methods described depends on the size of the sample taken for analysis and how the sample is taken. A sample must be large enough to be representative of the entire lot of corn and must be taken from all parts of the lot--whether bin, truck, or railroad car. One highly contaminated corn kernel may account for objectionable levels of aflatoxin in a 3,000-kernel (2-pound) sample. If only a 1- to 2-pound sample is collected, the one highly contaminated kernel could be missed. Usually from 5- to 10-pound samples are collected, but even larger ones would be better.

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WATER-INSOLUBLE STARCH XANTHATE

Preparation and Use in Heavy Metal Recovery

A water-insoluble starch xanthate offers industry a low cost product that removes and recovers heavy metals from wastewater. Previously, heavy metals had been effectively removed with a starch xanthate-cationic polymer complex (1,6,7) that allows metal recovery, but almost all cationic polymers are expensive. More traditional removal methods based on inorganic precipitation with lime, alum, or iron salts leave a sludge often placed in landfills. Leaching of the unrecovered metal to underground water and loss of metal resources result. Although precipitation as inorganic salts is inexpensive, recovery of the heavy metal for recycling is difficult.

Starch xanthate made from unmodified corn or wheat starch (2-5) is water soluble. Starch xanthate itself precipitates large amounts of mercury(II), but because almost all other metal xanthate salts are more soluble, removal is not so efficient as when a cationic polymer is included. The efficiencies of metal removal by starch xanthate alone can be greatly increased if the initial starch is crosslinked. Xanthation of a highly crosslinked starch gives an insoluble product. An insoluble starch xanthate lowers the concentration of practically all metals to levels below strict discharge limits.

Laboratory Preparation

A highly crosslinked starch (35.4 g.) is slurried in water (225 ml.), and aqueous alkali (0.2 M, 100 ml.) is added. This mixture is cooled to 4-20° C. in an ice bath and stirred 30 minutes. Carbon disulfide (5 ml.) is added and the mixture is stirred 4-16 hours. A stoppered water condenser is used to keep the carbon disulfide from evaporating. The slurry is filtered through a coarse sintered-glass funnel and the solid is washed with several portions of acetone (500 ml. total) and then ether (100 ml.). Weights of reactants and analyses of the products for several preparations are found in Table 1. The pale yellow solid is stored at 0° C. in a closed container. Under these conditions the products show no decomposition during 4 months storage.

Table 1.--Preparation and Analysis of Insoluble Starch¹ Xanthate

NaOH, ² g.	Carbon Disulfide, ³ ml.	Product wt., g.	% S, As-is	D.S. ⁴	% Ash ⁵	% H ₂ O ⁶
8	5	43.0	5.46	0.15	15.67	12.22
8	10	41.0	6.82	0.19	11.70	9.57
16	5	48.4	6.43	0.18	22.14	15.62
16	10	50.0	9.44	0.29	22.81	14.95

¹ Epichlorohydrin crosslinked starch (53-91E, The Hubinger Company, Keokuk, Iowa). 9.09% H₂O; 35.4 g. (0.2 mole, dry basis).

² 8 g. NaOH ~ 0.2 mole.

³ 5 ml. CS₂ ~ 0.08 mole.

⁴ % S = $\frac{6400 \text{ D.S.}}{162 + 98 \text{ D.S.}}$

⁵ % Ash includes sodium of xanthate and bound alkali in product.

⁶ % H₂O is uncorrected for xanthate decomposition during moisture analysis which was run at room temperature under vacuum for 2-3 hours.

For preparation of crosslinked starch xanthate on a commercial scale, the solid recovered on filtration probably would be spray or flash dried rather than dehydrated by solvents.

Heavy Metal Removal

Almost all heavy metals can be removed by the water-insoluble starch xanthate from water to levels below established discharge limits (Table 2). Each metal solution is treated with the water-insoluble starch xanthate to determine how much is required for effective removal. If the initial pH is 3, solid starch xanthate in the range of 0.037-0.0859 g./50 ml. is required for good removal. However, if the initial pH is greater than 5, stoichiometric quantities of xanthate (one xanthate group per metal ion) are sufficient. Since the solid starch xanthate is basic, the pH of the treated solution will increase, and effective removal is always obtained in the pH range of acceptable discharge.

Table 2.--Removal of Heavy Metals with Water-Insoluble Starch Xanthate

Metal	Initial ¹ Concn., µg./liter	pH, Initial	pH, ² 2 Hours	Residual Metal, µg./liter	Illinois Discharge Limit, µg./liter
Cu ⁺²	31,770	3.4	6.4	7	20
Ni ⁺²	29,350	3.2	7.7	19	1,000
Cd ⁺²	56,200	3.0	6.8	9	50
Pb ⁺²	103,600	3.1	7.3	25	100
Cr ⁺³	26,000	3.2	6.5	3	1,000
Ag ⁺	53,930	3.1	7.2	245	5
Zn ⁺²	32,680	3.1	7.5	46	1,000
Fe ⁺²	27,920	3.0	6.4	0	1,000
Mn ⁺²	27,470	3.3	9.0	1,630	1,000
Hg ⁺²	100,000	3.1	4.2	3	0.5

¹ A 50-ml. sample.

² Stir solution 2 hours before filtering.

A contact time as short as 5 minutes is sufficient for good removal. For example, a solution containing 31,770 µg./liter copper(II) was reduced to a residual level of 22 µg./liter copper(II) within 5 minutes and to a level of 20 µg./liter within 120 minutes. Salt (NaCl) concentrations of 0-10 percent have little influence on the effectiveness of the method. Residual metal concentrations are low with various degrees of substitution (D.S.) in the solid starch xanthates; however, the higher the D.S., the greater the metal-binding capacity.

Separation of Solid Starch Xanthate-Metal Precipitate

A solution (1,000 ml.) of copper(II) (31.77 mg./liter) at pH 3.2 was treated with solid starch xanthate (0.3 D.S.; 1.25 g.) to a final pH of 7. After the mixture stirred 2 hours, it was filtered and the air-dried precipitate weighed 1.02 g. (decrease in weight due to loss of bound base). The filtrate contained only 46 µg./liter of copper and had only 50 mg./liter chemical oxygen demand. A portion (0.20 g.) of the precipitate was treated with a few drops of concentrated nitric acid. The gold colored precipitate turned white and the solution blue. Water (5 ml.) was added and the mixture

was filtered and washed with water (20 ml.). The filtrate was diluted to 100 ml. and the solid was oven dried at 100° C. Copper analysis of the filtrate showed 62.44 mg./liter (calc. 62.35 mg./liter) and the solid crosslinked starch byproduct weighed 0.1526 g. (76.2 percent of 0.20 g. precipitate). The xanthate group was oxidized by the nitric acid to sulfate. When the xanthate group is added into the total weight, recovery is theoretical.

The copper nitrate or sulfate can be recycled back into the plant as-is or can be sent elsewhere for further purification and recovery.

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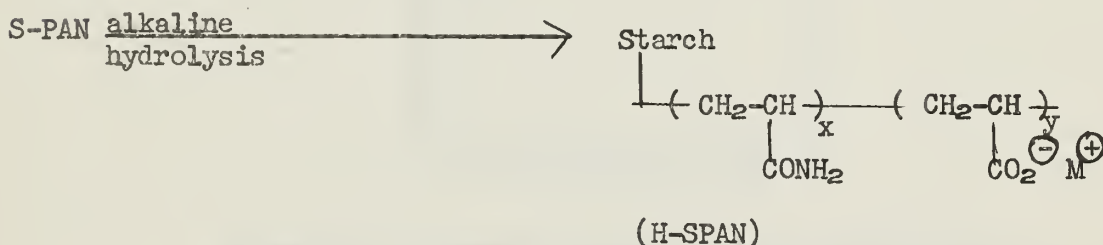
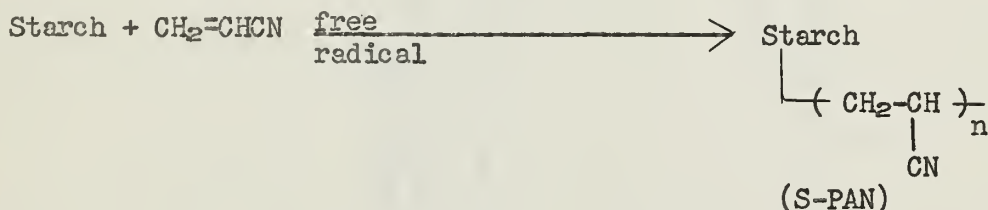
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HYDROLYZED STARCH-POLYACRYLONITRILE GRAFT COPOLYMERS

A new graft copolymer, developed at the Northern Regional Research Laboratory, has a backbone of starch with grafted branches which are made up of acrylamide and acrylic acid repeating units. A wide variety of compositions are possible, since the molecular weight of starch, the molecular weight of the grafts, the ratio of acrylamide to acrylic acid, and the frequency of grafting may be varied. These graft copolymers are synthesized by first graft polymerizing polyacrylonitrile onto starch and then subjecting the resulting polymer to alkaline hydrolysis.



Direct grafting onto starch of acrylamide-acrylic acid mixtures and alkaline hydrolysis of starch-polyacrylamide graft copolymers give products which are structurally similar to H-SPAN.

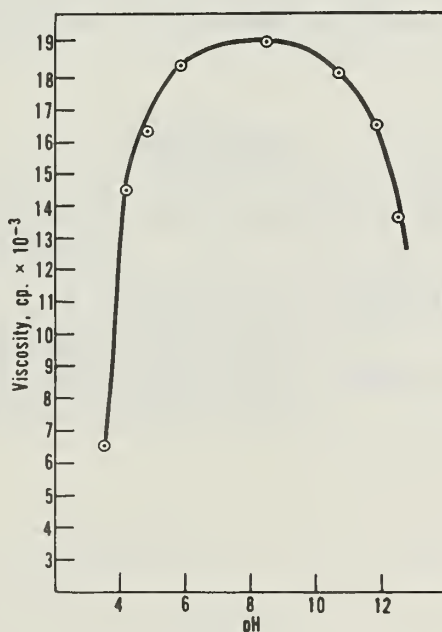
A typical composition for the S-PAN precursor is: 50% starch, 50% PAN (by wt.), \bar{M}_v of PAN: 800,000. A typical alkaline hydrolysis gives grafts which contain about equal amounts of acrylamide and acrylic acid.

The properties of H-SPAN depend on whether the acrylic acid moiety is present as the free acid or as the alkali metal carboxylate. In the free acid form, the graft copolymer has only limited solubility in water. Addition of alkali to give the metal carboxylate increases swelling and solubility of the graft copolymer. At a pH 6-7, a smooth highly viscous dispersion is obtained.

End Use Applications

Thickeners

The high viscosity of aqueous dispersions of H-SPAN is shown in the graph below.



Brookfield viscosity vs. pH of 1% dispersion of hydrolyzed starch polyacrylonitrile graft copolymer, 25° C, 30 rpm, and No. 4 spindle.

H-SPAN will also thicken water-organic solvent mixtures, such as ethanol-water (80:20) and methylene chloride-methanol-water (60:30:10).

Flocculants

Aqueous dispersions of H-SPAN in the carboxylate form may be used as flocculating agents for water purification. Laboratory tests have been conducted with various clay formulations, raw sewage, and coal slurries. H-SPAN has been effective in all systems examined.

Hydrophilic Gels

Aqueous dispersions of H-SPAN, in the carboxylate form, air dry to produce continuous films which will rapidly imbibe 200-300 times their weight in water. These films do not dissolve in excess water but form sheets of gel which are identical in shape but about 30 times larger in surface area than the original dry film. The gel structure may be destroyed mechanically (e.g., by colloid milling) to give a clear solution; however, air drying gives a film which, on hydration, yields a gel sheet similar to the original. Gel sheets will contract to a rubbery film in dilute mineral acid but will expand again in dilute alkali.

Hydrophilic gels from H-SPAN have ion exchange properties and also serve as insoluble supports for enzymes. If thin films of H-SPAN are formed on finely divided substrates, such as starch or clay, the water-holding capacity of the substrate is greatly increased due to the high affinity of the H-SPAN film for water.

References

Specific details on the preparation and thickening properties of H-SPAN may be found in the following references:

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LINSEED OIL

Curing-Antiscaling Emulsion for Concrete

For several years the Northern Regional Research Laboratory (NRRL) has conducted research on the use of linseed oil for coating concrete. This research includes studies both on curing concrete and on protecting concrete against scaling and spalling caused by freezing and thawing (4,5). Substantial savings can be realized by applying an NRRL boiled linseed oil emulsion as a curing compound shortly after placing concrete, and the antiscaling effect of this emulsion lasts for at least 2 years. This procedure eliminates cleaning, drying, and traffic control required when antiscaling agents are applied 14 to 30 days after curing.

After 2 years the pavement should be treated periodically with linseed oil. Such treatment may already be standard practice for pavement in some locations. Standard practice is to use the most economical form of linseed oil as an antiscaling agent. To date, linseed oil dissolved in a mineral spirits solvent has served this purpose (16). However, such a solution is flammable and is not a curing agent. The lack of flammability of the emulsion makes it preferable over the solution for coating enclosed areas, such as basements and underground garages.

Preparation of Emulsion: Composition of the NRRL emulsion (8,9) is as follows, with suggested limits:

	<u>Weight %</u>
Oil phase (50 ± 1 volume %)	
Boiled linseed oil	97.0 ± 1
Saturated tallow alcohols	3.0 ± 1
Water phase (50 ± 1 volume %)	
Water	99.60 ± 0.01
Sodium hydroxide	0.37 ± 0.01
Dipicolinic acid	0.03 ± 0.001

The saturated tallow alcohols are dissolved in boiled linseed oil at 140° F. Both sodium hydroxide and dipicolinic acid are dissolved in the water. The oil phase is slowly added to an equal volume of the water phase with good agitation (i.e., a 4-inch Cowles dissolver operating at 2,900 r.p.m.).

A note of caution: Do not add the water phase to the oil phase and do avoid beating in air while mixing. Finally, the emulsion is pumped through a two-stage homogenizer (such as one made by Manton-Gaulin or by Cherry-Burrell) at

4,000 p.s.i. The emulsion is stable through more than five freeze-thaw cycles (a cycle is 70° to 0° to 70° F.) and remains stable for more than 2 years.

According to laboratory tests, alternate formulations (10) yielding reduced water loss during curing and more durability afterwards can be obtained by substituting heat-bodied linseed oil or tung oil for 20 percent of the boiled linseed oil in the oil phase of the original emulsion. The heat-bodied linseed oil should have a Gardner Holdtviscosity Z8 (40,000 to 50,000 centipoises Brookfield).

Companies who have licensed patents assigned to the Secretary of Agriculture are listed in Table 1. Almost all these companies are in commercial production of the NRRL emulsions.

Water Retention: The NRRL emulsion passes the ASTM:C156 Water Retention Efficiency of Liquid Membrane-Forming Compounds for Curing Concrete (17), when it is applied at 175 square feet per gallon. The maximum loss allowed in this test is 0.055 gram per square centimeter per 72 hours. Five different commercial batches tested as follows: 0.044, 0.055, 0.045, 0.043, and 0.040 gram per square centimeter per 72 hours.

The alternate emulsions (10) meet the ASTM test at 200 square feet per gallon with losses as low as 10 to 22 milligrams per square centimeter. They also pass the U.S. Army Corps of Engineers CRD-C302-68 Method of Test for Sprayability and Unit Moisture Loss Through the Membrane Formed by a Concrete Curing Compound. It is being determined in the field whether increased durability justifies the slightly greater cost of these formulas.

Curing Application: The emulsion should be applied as soon as the concrete is finished (broomed, dragged, or troweled). The preferred method of application is with an airless spray gun or a wand like that used for orchard spraying. An ordinary paint spray gun can be used with an air pressure of about 30 p.s.i.

The nominal rate of application is 175 square feet per gallon for broomed surface concrete (200 square feet per gallon for the alternate emulsions).

Antiscaling Application: If the emulsion is intended as an antiscaling agent, it should be applied when the concrete is at least 2 weeks old and preferably 4 weeks. It can be applied with beneficial results to older concrete, even to surfaces that have started to scale. Any surfaces should be clean and dry before coating. Two coats are preferable to gain more uniform application. The coats should total about 225 square feet per gallon for both boiled linseed oil and alternate emulsions. Rate of application depends on porosity and roughness of the concrete surface. Care should be taken to avoid an excess of oil because this condition will temporarily lower wet skid resistance (12).

Abrasion Resistance: When applied as a curing compound, the NRRL emulsion slows down hardening of the surface. Light traffic is permissible (such as that required to cut joints) in 5 to 24 hours, but heavy traffic should be kept off for 72 hours. At 28 days, hardness is normal and continues to increase thereafter. Research at

the Northern Regional Laboratory tends to confirm results reported by the California Division of Highways (3), which states that linseed oil increases the abrasion resistance of concrete more than any other material tested.

Penetration: The penetration of linseed oil curing and antiscaling compounds into the surface of concrete may be related to their ability to protect concrete from freeze-thaw cycles and deicing chemicals (13,18). On the one hand, conventional curing agents, which do not protect, tend to form a film on the surface and do not penetrate into the concrete. On the other hand, linseed emulsions penetrate when used as either a curing or antiscaling agent. The Northern Regional Laboratory, in cooperation with the National Flaxseed Processors Association, has developed a simple test for determining penetration of linseed emulsions and solutions into concrete (6,7).

Practical Studies on Sidewalks: NRRL's linseed oil emulsion has been used to cure concrete sidewalks in Peoria, Ill., and in Washington, D.C. (11,14). Applications at the Northern Laboratory in April, May, and June 1963, were the first outside curing tests. The results were reported as "pop-outs" within 100 square feet. A piece of concrete pops out apparently when a porous rock beneath the surface absorbs water, freezes, and expands. After 39 applications of salt on sidewalks between the spring of 1963 and the spring of 1965, emulsion-cured concrete averaged 20 pop-outs; membrane-cured concrete, 152; plastic-cured concrete, 157; and air-cured concrete, 222.

That part of the Washington, D.C., sidewalk cured under polyethylene sheeting has had to be replaced because of damage from heavy salting. The linseed oil emulsion-cured area is still in excellent condition.

Curing of Bridge Decks: In 1966, engineers from Wichita, Kansas, specified the NRRL emulsion for city construction. It has now been placed on a total of 11 projects in Kansas under weather conditions varying from freezing to hot and windy.

In 1970, the Oklahoma State Highway Department (1,2,15) became the first to specify curing bridge decks with the oil-in-water emulsion developed and patented by NRRL. Concrete in 138 bridges was emulsion-cured after Oklahoma began tests in 1968 in cooperation with the U.S. Department of Agriculture and the U.S. Department of Transportation. Emulsion curing was specified for 25 bridge contracts let between December 1970 and May 1971. In 1971, Arkansas included the emulsion in its specifications for curing bridges.

Emulsion Curing and Interaction with Later Treatments: A linseed oil coating increases adhesion of traffic paints. Bituminous overlay can be made on linseed oil-treated concrete with no loss of adhesion if a tack coat is first applied. Carborundum and other finishes can be put on concrete that has been cured with linseed oil emulsion.

Savings: In addition to increasing the life of concrete, Table 2 illustrates savings in labor and materials resulting from the linseed oil emulsion method

of curing and protecting concrete. Although costs vary widely, about \$1.00 a square yard is saved by applying a linseed oil emulsion instead of moist curing followed by a linseed oil antiscaling treatment. If membrane curing is followed by linseed oil antiscaling treatment, the saving is slightly less. One company using the emulsion exclusively to cure outdoor concrete estimates its savings between \$0.79 to \$0.81 per square yard. The contractor returned \$0.26 per square yard to the company on his first use of the emulsion method.

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Mention of firm names or trade products is made for information only and does not imply that they are endorsed or recommended by the U.S. Department of Agriculture over other firms or similar products not mentioned.

Table 1.--Licenses Granted on Concrete Curing Patents issued to William L. Kubie and assigned to Secretary of Agriculture

Licensee	U.S. 3,140,191 (Issued 7-7-64)	U.S. 3,228,777 (Issued 1-11-66)	Serial No. 183,652 (Filed 9-24-71)
Carter-Waters Corp. Kansas City, Mo.		7-21-66	
Darling and Company Chicago, Ill.	10-5-71	3-27-68	1-28-72
Con-Cure Co. Tulsa, Okla.	12-4-70	12-4-70	
Nu-Pro, Inc. Oklahoma City, Okla.	5-17-71	5-17-71	
Protex Industries, Inc. Denver, Colo.	12-29-71	12-29-71	5-22-72
Chemex Industries, Inc. Tampa, Fla.		3-9-72	
W. R. Meadows, Inc. Elgin, Ill.		4-10-72	
PVO International Inc. Richmond, Calif.	8-16-72	8-16-72	8-16-72
Polyguard Pipeline Products, Inc. Pryor, Okla.	10-20-72	10-20-72	10-20-72
Custom Chemicals Blending & Mfg. Co. Joplin, Mo.	4-3-73	4-3-73	4-3-73

Table 2.--Concrete Curing, Protecting Comparisons

Wet curing, followed 30 days later with antiscaling steps ^{1/}	Membrane curing, followed 30 days later with antiscaling steps ^{1/}	Linseed emulsion curing-antiscaling 5 hours ^{1/}
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CURING

1a. Spread plastic sheets, burlap mats as soon as they will not mar concrete surface, usually about 5 hr. after placing concrete	Spray with curing compound when free water disappears. Leaves concrete ready for sawing. May interfere with painting (traffic lines) and finishing	Spray with linseed oil emulsion as soon as free water disappears, immediately to 5 hr. after placing. Leaves concrete ready for sawing, painting (lines), or finishing.
1b. Burlap must be kept wet by repeated spraying with water (extra steps)		Protects against freeze-thaw damage after 2 years. Eliminates 6 steps

SAWING

2. Remove plastic or burlap 5 to 24 hr. after placing concrete	2. Eliminated	2. Eliminated
3. Saw joints	3. Saw joints	3. Saw joints
4. Replace plastic or burlap immediately (sometimes forgotten)	4. Eliminated	4. Eliminated
5. Plastic or burlap usually removed at end of 3 days to get it out of the way. Longer curing better	5. Eliminated	5. Eliminated

ANTISCALING PROTECTION--THREE EXTRA STEPS

6. About 30 days after step 1a or 1b concrete is cleaned	6. Cleaning as in wet curing	6. Eliminated
7. First application of flammable antiscaling compound	7. First application of antiscaling compound as in wet curing	7. Eliminated
8. Second application of flammable antiscaling compound	8. Second application of antiscaling compound as in wet curing	8. Eliminated

^{1/}

Time elapsed between placing of concrete and start of final three steps.

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UNITED STATES DEPARTMENT OF AGRICULTURE
AGRICULTURAL RESEARCH SERVICE
Northern Regional Research Laboratory
Peoria, Illinois 61604 DS

POWDERED ELASTOMERS

Starch Xanthide-Encased SBR 1502

New powdered elastomers developed at the Northern Regional Research Laboratory consist of latex particles encased in either starch or flour derivatives that serve as rubber-reinforcing agents.^{1,2} Selected powdered elastomers have been prepared on a pilot-plant scale.

Powdered elastomers offer substantial savings to rubber processors because they can be fabricated into rubber articles by powder processing techniques common in the plastics industry. All ingredients of a compounder's recipe can be premixed in a high-intensity Henschel-type mixer to give a free-flowing powder. The premixed compound can then be fed directly to an extruder or injection molding machine for high-speed automated production of rubber goods. Alternatively, existing processes and equipment may be adapted for use of powder blended compounds with large savings in manufacturing costs. In addition, an estimated savings in capital investment of more than 50 percent can be realized by designing new rubber fabrication plants for powder in place of baled elastomers.³

The following data are for a low-cost, powdered SBR elastomer designed for general-purpose usage. Also given is the procedure to be followed in making this powdered elastomer from SBR 1502 and starch xanthate:

SBR 1502 Powder

Composition

SBR 1502 elastomer	100 parts
Starch xanthide (SX), starch basis	3, 5, or 10 parts
Total	103, 105, or 110 parts

Particle size

	<u>3 phr SX</u>	<u>5 phr SX</u>	<u>10 phr SX</u>
Percent through 4 mesh	84	88	92
8 mesh	41	59	70
12 mesh	16	35	56

Particles greater than the 4 mesh size are agglomerates that reduce to a much smaller size when blended in a Henschel-type mixer with compounding ingredients.

Compounded Properties

Since the powders may be directly substituted for slab rubber, a standard formulation was tested to compare properties of samples based on slab rubber with those based on powdered rubber.

Recipes

	Parts by weight				
	A	B	C	D	E
SBR 1502 (slab)		200	200		
SBR 1502 (3 phr SX- encased powder)	200			200	206
IRB #3 carbon black	80	80	40	40	34
ZnO	10	10	10	10	10
Sulfur	4	4	4	4	4
Stearic acid	3	3	3	3	3
PBNA	2	2	2	2	2
Benzothiazyl disulfide	4	4	4	4	4
Tetramethylthiuram disulfide	0.2	0.2	0.2	0.2	0.2

Compound Physical Properties

	A	B	C	D	E
Tensile strength	3,600	3,400	1,800	1,640	1,600
Elongation	380	400	490	390	410
300% Modulus	2,920	2,400	750	1,000	860
IRHD Hardness	75	65			
Rebound	46	48			

Preparation of Powdered Rubber

Materials

Reagents required are the elastomer latex, starch xanthate, sodium nitrite, and sulfuric acid.

Starch xanthate is prepared by treating starch with base and carbon disulfide. Methods have been reported for continuous production of starch xanthate in a high-solids reactor⁴ and for a batch process.⁵ A typical laboratory procedure for preparing starch xanthate of DS 0.35 is:

Corn starch (180 g., 10% H₂O) slurried in water (1 liter) is gelatinized with sodium hydroxide (40 g. in 345 ml. H₂O) and then carbon disulfide (57 g.) is added during continuous mixing with an air stirrer. The mixture is then stored at 5° C. for 2 hours. The resulting starch-xanthate solution is ready after 2 hours of storage but may be kept for several days before use. When starch xanthate is treated with an oxidant, it forms crosslinked insoluble SX.

Method (for 5 phr SX-encased powdered rubber)

The SBR 1502 latex (1 kg., 20% solids) is mixed with starch xanthate solution (100 g., 10% starch) and sodium nitrite (0.5 g.). The mixture is stirred (air stirrer, 400 r.p.m. to give turbulent mixing) and M sulfuric acid is added slowly until pH 2.5 is reached. The fine crumb that precipitates is drained through cheesecloth and washed once with water and three times with methanol or ethanol. The alcohol-wet crumb is dried at 60-70° C. in vacuum for 6-16 hours.

Current studies are directed toward modification of the method to permit water washing-air drying of the precipitated SX-encased latex. Success has been realized with this modification for 20 phr SX-csSBR 1713.

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The information presented is believed to be accurate but carries no guarantee or responsibility on the part of the Northern Laboratory. None of this information can be taken as a recommendation to use the materials described in violation of patents. Mention of firm names or commercial products does not constitute an endorsement by the U.S. Department of Agriculture.

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UNITED STATES DEPARTMENT OF AGRICULTURE
AGRICULTURAL RESEARCH SERVICE
Northern Regional Research Laboratory
Peoria, Illinois 61604WATER-INSOLUBLE STARCH XANTHATEPreparation and Use in Heavy Metal Recovery

A water-insoluble starch xanthate offers industry a low cost product that removes and recovers heavy metals from wastewater. Previously, heavy metals had been effectively removed with a starch xanthate-cationic polymer complex (1,6,7) that allows metal recovery, but almost all cationic polymers are expensive. More traditional removal methods based on inorganic precipitation with lime, alum, or iron salts leave a sludge often placed in landfills. Leaching of the unrecovered metal to underground water and loss of metal resources result. Although precipitation as inorganic salts is inexpensive, recovery of the heavy metal for recycling is difficult.

Starch xanthate made from unmodified corn or wheat starch (2-5) is water soluble. Starch xanthate itself precipitates large amounts of mercury(II), but because almost all other metal xanthate salts are more soluble, removal is not so efficient as when a cationic polymer is included. The efficiencies of metal removal by starch xanthate alone can be greatly increased if the initial starch is crosslinked. Xanthation of a highly crosslinked starch gives an insoluble product. An insoluble starch xanthate lowers the concentration of practically all metals to levels below strict discharge limits.

Laboratory Preparation

A highly crosslinked starch (35.4 g.) is slurried in water (225 ml.), and aqueous alkali (0.2 M, 100 ml.) is added. This mixture is cooled to 4-20° C. in an ice bath and stirred 30 minutes. Carbon disulfide (5 ml.) is added and the mixture is stirred 4-16 hours. A stoppered water condenser is used to keep the carbon disulfide from evaporating. The slurry is filtered through a coarse sintered-glass funnel and the solid is washed with several portions of acetone (500 ml. total) and then ether (100 ml.). Weights of reactants and analyses of the products for several preparations are found in Table 1. The pale yellow solid is stored at 0° C. in a closed container. Under these conditions the products show no decomposition during 4 months storage.

Table 1.--Preparation and Analysis of Insoluble Starch¹ Xanthate

NaOH, ² g.	Carbon Disulfide, ³ ml.	Product wt., g.	% S, As-is	D.S. ⁴	% Ash ⁵	% H ₂ O ⁶
8	5	43.0	5.46	0.15	15.67	12.22
8	10	41.0	6.82	0.19	11.70	9.57
16	5	48.4	6.43	0.18	22.14	15.62
16	10	50.0	9.44	0.29	22.81	14.95

¹ Epichlorohydrin crosslinked starch (53-91E, The Hubinger Company Keokuk, Iowa). 9.09% H₂O; 35.4 g. (0.2 mole, dry basis).

² 8 g. NaOH ~0.2 mole.

³ 5 ml. CS₂ ~0.08 mole.

⁴ % S = $\frac{6400 \text{ D.S.}}{162 + 98 \text{ D.S.}}$

⁵ % Ash includes sodium of xanthate and bound alkali in product.

⁶ % H₂O is uncorrected for xanthate decomposition during moisture analysis which was run at room temperature under vacuum for 2-3 hours.

For preparation of crosslinked starch xanthate on a commercial scale, the solid recovered on filtration probably would be spray or flash dried rather than dehydrated by solvents.

Heavy Metal Removal

Almost all heavy metals can be removed by the water-insoluble starch xanthate from water to levels below established discharge limits (Table 2). Each metal solution is treated with the water-insoluble starch xanthate to determine how much is required for effective removal. If the initial pH is 3, solid starch xanthate in the range of 0.037-0.0859 g./50 ml. is required for good removal. However, if the initial pH is greater than 5, stoichiometric quantities of xanthate (one xanthate group per metal ion) are sufficient. Since the solid starch xanthate is basic, the pH of the treated solution will increase, and effective removal is always obtained in the pH range of acceptable discharge.

Table 2.--Removal of Heavy Metals with Water-Insoluble Starch Xanthate

Metal	Initial ¹ Concn., µg./liter	pH Initial	pH, ² 2 Hours	Residual Metal µg./liter	Illinois Discharge Limit, µg./liter
Cu ⁺²	31,770	3.4	6.4	7	20
Ni ⁺²	29,350	3.2	7.7	19	1,000
Cd ⁺²	56,200	3.0	6.8	9	50
Pb ⁺²	103,600	3.1	7.3	25	100
Cr ⁺³	26,000	3.2	6.5	3	1,000
Ag ⁺²	53,930	3.1	7.2	245	5
Zn ⁺²	32,680	3.1	7.5	46	1,000
Fe ⁺²	27,920	3.0	6.4	0	1,000
Mn ⁺²	27,470	3.3	9.0	1,630	1,000
Hg ⁺²	100,000	3.1	4.2	3	0.5

¹ A 50-ml. sample.

² Stir solution 2 hours before filtering.

A contact time as short as 5 minutes is sufficient for good removal. For example, a solution containing 31,770 µg./liter copper(II) was reduced to a residual level of 22 µg./liter copper(II) within 5 minutes and to a level of 20 µg./liter within 120 minutes. Salt (NaCl) concentrations of 0-10 percent have little influence on the effectiveness of the method. Residual metal concentrations are low with various degrees of substitution (D.S.) in the solid starch xanthates; however, the higher the D.S., the greater the metal-binding capacity.

Separation of Solid Starch Xanthate-Metal Precipitate

A solution (1,000 ml.) of copper(II) (31.77 mg./liter) at pH 3.2 was treated with solid starch xanthate (0.3 D.S.; 1.25 g.) to a final pH of 7. After the mixture stirred 2 hours, it was filtered and the air-dried precipitate weighed 1.02 g. (decrease in weight due to loss of bound base). The filtrate contained only 46 µg./liter of copper and had only 50 mg./liter chemical oxygen demand. A portion (0.20 g.) of the precipitate was treated with a few drops of concentrated nitric acid. The gold colored precipitate turned white and the solution blue. Water (5 ml.) was added and the mixture

was filtered and washed with water (20 ml.). The filtrate was diluted to 100 ml. and the solid was oven dried at 100° C. Copper analysis of the filtrate showed 62.44 mg./liter (calc. 62.35 mg./liter) and the solid crosslinked starch byproduct weighed 0.1526 g. (76.2 percent of 0.20 g. precipitate). The xanthate group was oxidized by the nitric acid to sulfate. When the xanthate group is added into the total weight, recovery is theoretical.

The copper nitrate or sulfate can be recycled back into the plant as-is or can be sent elsewhere for further purification and recovery.

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